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Effects of Soil Composition on Zn Speciation in Drainage Waters from Agricultural Soils

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Abstract. The influence of Zn speciation on Zn transport by drainage from different soils to surface water is examined in a stream catchment in an agricultural area. Drainage waters were collected from two types of soils, a mineral soil (MS) and a soil rich in organic matter (OS) by means of artificial drainage pipes. The speciation of dissolved Zn in the stream and the drainage waters was determined using ligand-exchange and voltammetry. About 50–95% of dissolved Zn is bound in strong complexes, and the free Zn^{2+} ion concentration is in the range of 1–16% of dissolved Zn. A substantial part of Zn is present in weaker organic or inorganic complexes. The simulated Zn speciation using the WHAM VI model is compared to the determined speciation. Free Zn^{2+} concentrations predicted by the WHAM VI model are generally higher than the analytically determined free Zn^{2+}, but are mostly within the same order of magnitude. Effects of different soil organic matter content on Zn speciation and transport are discussed. Zn speciation in the drainage at the OS site is influenced by the distribution of organic matter between the solid and solution phase. The abundant organic Zn complexes in solution contribute to facilitate Zn transport from soil into surface waters, through the drainage at the OS site. Drainage from the OS site contributes about twice as much Zn input to the receiving water as the MS soil, as related to specific area. The mineral soil contains much lower organic matter, and a part of Zn bound with inorganic phases can hardly be released by dissolved organic ligands, leading to much higher Zn retention at the MS site.

Key words: agricultural soil, soil drainage, surface water, Zn input, Zn speciation, Zn transport by drainage

1. Introduction

The metals Zn and Cu are often added to livestock forage due to their anti-microbial and growth promoting properties, with significant concentrations of these metals ending up in the manure (Menzi et al., 1999; Nicholson et al., 1999; Xue et al., 2000). Long-term intensive application of livestock manure with

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high Cu and Zn concentrations often exceeds the uptake by grass or crops and therefore leads to the accumulation of manure-borne metals in the soils and also results in elevated metal concentrations in the receiving waters (Aldrich et al., 2002; Xue et al., 2000, 2003). It is therefore important to understand factors that affect the mobility of metals from soils, which have received intensive application of manure with relatively high metal concentrations, to the drainage and receiving surface waters. The mechanisms controlling metal transfer from manure-amended soils to water should be investigated.

Metal retention or mobility in soils is strongly affected by metal speciation (Aldrich et al., 2002; Weng et al., 2002). On one hand, the metals undergo complexation by soil organic matter, adsorption or precipitation in the soil and are retained in the topsoil. On the other hand, metals in the soils migrate by percolation and seeping together with the soil solution to surface and groundwater systems. Major species of Zn in soil matrix rich in organic matter are probably organic complexes, which are either adsorbed to solid phases or are present in the soil solution. High organic matter content may adsorb higher metal fractions than mineral clay even in sandy soil (Weng et al., 2002). Of course, for soils with low organic matter content and high pH, metal binding to minerals (hydroxides, clay minerals) can also be important (Zachara et al., 1992). Therefore, the metal mobility from organic rich soil depends on the competition between soluble soil organic matter and particulate-bound soil organic matter. The soil characteristics, such as permeability and seeping of soil water, play an important role. Our previous work showed that two soils with distinct properties in the same catchment contribute different metal loads to surface waters, in spite of similar metal inputs (Xue et al., 2003). Retention and release of Zn appeared to differ between soils with different organic contents. Weng et al., (2002) have found in a sandy soil that the dissolved organic complexes are generally more significant for Cu than for Zn in their solubility and mobility.

In the present study, we intend to compare Zn speciation in drainage waters from two soils in the same catchment, a mineral soil (MS) and a dark colored soil rich in organic matter, and to examine the effects of organic complexation of Zn on its downward migration and on its transport with drainage to the receiving small stream (Kleine Aa). In this study, we investigate the speciation of Zn in the receiving stream water and the artificial drainage-aided soil leachate, using ligand-exchange and differential pulse anodic stripping voltammetry (DPASV). The drainage waters represent real soil solutions leaching from different soils. The determined Zn speciation is compared with results from modeling using the WHAM model. Possible causes of the discrepancies between the determined and modeled speciation are discussed. The effects of soil composition and their properties with regard to water leaching on the metal speciation and their migration and transport through drainage are also discussed.

2. Methods

2.1. DESCRIPTION OF CATCHMENT AND SAMPLING SITES

The study area is a relatively small catchment, with a total area of 6.9 km^2. The entire catchment is drained by the stream Kleine Aa flowing into Lake Sempach in central Switzerland. The drainage basin comprises maintained grassland (60%), arable land (15%), forestry (15%) and urban development (10%), with 75% of the total basin area under intensive farming. The grassland in the catchment is managed for dairy farming, with a high average livestock density, equivalent to about 3 dairy-cow ha^{-1} (Gächter et al., 1998). Cattle manure is applied up to six times per year, with at a typical rate of 30 m^3 ha^{-1} per application. The slurry manure contains relatively high level of Zn (6–45 mg Zn L^{-1}) (Xue et al., 2000). Manure application, according to the volume of cattle slurry applied, equates to Zn inputs to the soils ranging from 100 to 800 mg Zn m^{-2} yr^{-1}. About 40% of the total catchment area is artificially drained for more than half a century. The transport of nutrients and metals from the catchment into the receiving water Lake Sempach is probably accelerated by this artificial drainage. The majority of the soil (90%) in the catchment (4.7 km^2) has developed from glacial till (Würm glaciations) and molasses, which is shallow, loamy district eutrochrept of low permeability. The soil in the remaining 10% of the catchment area (0.52 km^2) is dark colored organic soil, developed from artificially drained marsh-land. For comparison, another stream in the catchment area of Lake Sempach is also sampled, Greuelbach, which is much less affected by farming and by the presence of livestock.

Water samples were collected from the drainage pipes from a ''mineral soil'' (MS) and an ''organic soil'' (OS) area. Water samples were also collected from the stream Kleine Aa, which is receiving the water from the drainage pipes, and from the stream Greuelbach, both nearby the inlet to Lake Sempach during the period of October 1999 to February 2000.

2.2. SAMPLING

Water samples from the streams were collected manually using polyethylene bottles (1 L) from the subsurface flowing water near the center of the stream. Water samples from the drainage pipes were collected manually with polyethylene bottles (500 mL) from outlets of the drainage pipes. The outlets are located on the river banks leading from MS or OS into the river. The collecting time intervals for individual samples depended on the drainage flow rate, which is related to the weather conditions, and ranged from about 1 to 10 min.

All sampling and filtration equipment was soaked in 0.01 M HNO_3, rinsed with double distilled water and stored in sealed polyethylene bags. The water sampling bottles were acid-washed and the water samples were stored

at 4 °C until analysis. Within a few hours after collection, a liter of each sample was filtered through a cellulose acetate membrane filter (0.45 μm, Whatman) into an acid-washed polyethylene bottle. An aliquot (ca. 600 mL) of each filtered sample was kept for Zn speciation measurements within 2 days. Another aliquot (100 mL) was preserved by acidifying to pH < 2, using Aristar HNO_3, for total dissolved metal measurement. A further 200-mL aliquot of each water sample was filtered through a glass fiber filter (0.45 μm, Whatman) into an acid-washed glass bottle for dissolved organic carbon (DOC) determination.

Collection and treatment of the soil columns from the two soil areas MS and OS have been described elsewhere (Xue et al., 2003).

2.3. ANALYTICAL METHODS

Total dissolved Zn in the water samples was analyzed in duplicates by inductively coupled plasma mass spectroscopy (ICP-MS, Perkin-Elmer SCIEX ELAN 5000), with a detection limit of 0.05 μg L^{-1} Zn. Total metal concentrations in digested soil were determined by ICP-OES (Spectro), with a detection limit of 0.01 mg L^{-1} for Zn. All the metal concentrations presented are average values of the duplicates.

The pH values of the water samples were measured on-site and in the laboratory with a Metrohm 704 pH meter. Dissolved organic carbon (DOC) of the water samples were measured by combustion at 680 °C on a Shimadzu TOC-500 analyzer.

Zn speciation in stream and drainage waters was determined by a technique of ligand-exchange with EDTA (ethylenediaminetetraacetate) and DPASV (differential pulse anodic stripping voltammetry) (Xue and Sigg, 1994; Xue et al., 2000). The labile Zn concentration in a sample (without or with 10–30 nM EDTA) was determined by DPASV measurement after Zn additions. All the titration series were kept at room temperature (21 ± 1 °C) overnight for longer than 15 h to reach equilibrium in presence of EDTA. MOPS (3-morpholinopropanesulfonic acid) buffer was used to keep the pH close (± 0.1 pH) to the natural values at the sampling sites (see Tables).

The measurements of labile Zn were performed with a hanging mercury drop electrode, an Ag/AgCl reference electrode, and a graphite counter electrode in a Metrohm VA 647 stand combined with a Metrohm VA 646 Processor. The conditions of DPASV measurement were 5 min pre-purging with N_2, deposition at −1.2 V for 2 min, scanning from −1.2 V to −0.8 V at pulse height 50 mV with scan rate 10 mV s^{-1} at room temperature (21 ± 1 °C).

The free Zn ionic concentration was evaluated by measuring labile Zn after equilibration with 10–30 nM EDTA. Briefly, EDTA is used as a competing ligand which forms DPASV non-labile complexes. The labile species

include free metal ions [Zn^{2+}], inorganic $\sum[ZnI_{in}]$ and weak organic complexes $\sum[ZnL_i]_{lab}$. The addition of EDTA modifies the mass balance by forming additional non-labile species, therefore the fraction of [Zn^{2+}] to $[Zn]_T$ measured during the metal titration is not the same with or without EDTA. If the added EDTA concentration just competes with the labile inorganic and organic complexes, the strong organic complexes $\sum[ZnL_i]_{nl}$ remain constant, and [ZnEDTA] is measured at any given total Zn concentration as the difference of labile Zn concentrations without and with EDTA addition. The free Zn ion concentration in the presence of EDTA can be calculated from the [ZnEDTA] at any given total Zn concentration:

$$[Zn^{2+}] = [ZnEDTA]/\alpha_{EDTA}, \quad (1)$$

where the complexation coefficient α_{EDTA} is the product of the calculated free EDTA concentration and the complex stability constant of ZnEDTA. The free EDTA concentration is calculated from the mass balance of total EDTA minus ZnEDTA complex, taking into account EDTA protonation and major cation (Ca and Mg) complexation. The competition of other trace metal complexes was ignored because of their relative low concentrations. This coefficient is usually in the range $\alpha_{EDTA} = 6\text{-}30$ with the addition of $1 \times 10^{-8} - 1 \times 10^{-7}$ M EDTA under typical natural freshwater conditions. $[Zn^{2+}]_{amb}$, is estimated by interpolating to the original condition at ambient total Zn concentration.

The inorganic complex concentration is estimated from the product of $[Zn^{2+}]_{amb}$ and the inorganic complexation coefficient, and the weak (labile) organic complex concentration from the mass balance of labile Zn at ambient condition. The strong organic complexes $\sum[ZnL_i]_{nl}$ are assumed to be simply equal to the non-labile Zn concentration in the original water sample without EDTA.

2.4. SPECIATION CALCULATIONS WITH WHAM VI

To compare model predictions with the measurements of Zn complexation, we simulated the data using the WHAM Model VI for ion binding to humic substances (Tipping, 1998). For modeling calculations, all the default parameters of the model were used, and the input data were taken from the determined water composition (Xue et al., 2003), as listed in Table I. DOC in freshwaters is mostly composed of fulvic acid. Therefore, the model calculations were carried out with the assumption that all DOC was colloidal FA, and the FA contains about 50% of organic carbon, therefore the amount of colloidal FA equal to $2 \times$ DOC. The total carbonate concentration was estimated from alkalinity instead of input pCO_2. Major cations Ca, Mg, Fe were taken into account for competition, total PO_4^{3-} concentration was also

Table I. Input composition for the simulation by Model WHAM VI*

Sampling site	Sampling date	Description	Colloidal FA g/L	Mg (M) Total	Ca (M) Total	Fe(III) (M) Total	Cu(II) Total	Zn(II) (M) Total	CO_3 (M) Total	PO_4 (M) Total
Kleine Aa	4-Oct-99	KA05Oct	0.0112	4.00E−04	2.80E−03	1.29E−06	5.98E−08	3.52E−08	6.10E−03	2.75E−06
Kleine Aa	25-Oct-99	KA 26Oct	0.0092	5.30E−04	2.79E−03	1.37E−06	1.34E−07	2.22E−07	6.70E−03	2.38E−06
Kleine Aa	9-Nov-99	KA 10Nov	0.0174	2.90E−04	1.98E−03	2.11E−06	7.24E−08	9.79E−08	4.20E−03	1.31E−05
Kleine Aa	24-Nov-99	KA25Nov	0.0096	4.50E−04	2.75E−03	4.42E−07	3.93E−08	3.52E−08	6.50E−03	1.76E−06
Kleine Aa	31-Jan-00	KA01Feb	0.0096	5.00E−04	3.10E−03	6.30E−07	2.99E−08	1.84E−08	6.40E−03	1.60E−06
Kleine Aa	14-Feb-00	KA15Feb	0.0088	3.60E−04	2.23E−03	7.21E−07	3.15E−08	1.99E−08	6.00E−03	1.36E−06
Greuelbach	4-Oct-99	GB05Oct	0.0042	3.00E−04	2.10E−03	3.04E−08	1.89E−08	2.45E−08	4.40E−03	1.01E−07
Greuelbach	25-Oct-99	GB26Oct	0.0036	3.90E−04	1.85E−03	5.04E−08	7.03E−08	2.45E−07	4.10E−03	1.81E−07
Greuelbach	9-Nov-99	GB10Nov	0.0058	2.80E−04	2.42E−03	4.12E−07	2.83E−08	5.05E−08	5.50E−03	9.89E−07
Greuelbach	24-Nov-99	GB25Nov	0.0052	3.20E−04	2.16E−03	8.00E−08	1.73E−08	2.60E−08	5.00E−03	1.33E−07
Greuelbach	31-Jan-00	GB01Feb	0.0030	2.50E−04	1.84E−03	5.02E−08	1.10E−08	3.06E−09	5.00E−03	1.98E−07
Greuelbach	14-Feb-00	GB15Feb	0.0030	3.10E−04	2.21E−03	5.80E−08	1.10E−08	9.18E−10	4.90E−03	1.53E−07
Mineral soil drainage	4-Oct-99	MS05Oct	0.0054	2.00E−04	3.00E−03	1.00E−07	2.99E−08	2.45E−08	7.20E−03	1.18E−06
Mineral soil drainage	9-Nov-99	MS10Nov	0.0094	1.50E−04	2.15E−03	8.42E−07	3.92E−08	6.88E−08	5.80E−03	4.55E−06
Mineral soil drainage	24-Nov-99	MS25Nov	0.0052	1.90E−04	2.68E−03	1.00E−07	2.52E−08	4.74E−08	6.90E−03	8.91E−07
Mineral soil drainage	14-Feb-00	MS15Feb	0.0044	1.70E−04	2.52E−03	1.16E−07	1.57E−08	3.06E−09	6.50E−03	6.11E−07
Organic soil drainage	4-Oct-99	OS05Oct	0.0656	2.00E−04	1.00E−03	1.53E−05	9.91E−08	9.33E−08	3.80E−03	6.00E−07
Organic soil drainage	9-Nov-99	OS10Nov	0.0406	7.00E−05	3.90E−04	1.20E−05	1.79E−07	3.26E−07	1.30E−03	2.43E−06
Organic soil drainage	24-Nov-99	OS25Nov	0.0848	1.10E−04	7.40E−04	1.43E−05	1.48E−07	3.15E−07	2.00E−03	1.66E−06
Organic soil drainage	31-Jan-00	OS01Feb	0.0784	1.00E−04	6.60E−04	2.05E−05	1.10E−07	2.65E−07	2.20E−03	8.08E−07
Organic soil drainage	14-Feb-00	OS15Feb	0.0760	9.00E−05	6.10E−04	1.96E−05	1.62E−07	3.35E−07	1.70E−03	9.98E−07

* The measured dissolved concentrations (< 0.45 μm) are used as total metal input in WHAM.

applied in the simulation. Temperature is automatically filled with 298 K, which does not much differ from the measurement condition. The model simulations yield concentrations of Zn^{2+}, of inorganic complexes and of FA-bound Zn, which can be compared to the experimentally determined Zn^{2+}, inorganic and organic complexes. No distinction between labile and non-labile organic complexes is obtained from the simulation. For comparison, it can be either assumed that FA-bound complexes correspond to the non-labile strong organic complexes, or that they are the sum of non-labile and labile organic complexes.

3. Results and Discussion

3.1. SPECIATION OF DISSOLVED ZN IN DRAINAGE AND RIVER WATERS

Table II lists the dissolved Zn speciation in the drainage waters from MS and OS, and Table III lists the dissolved Zn speciation in the receiving waters of Kleine Aa and in Greuelbach.

The total dissolved Zn in the OS drainage is much higher than in the streams, up to 9–13 times higher. The total dissolved Zn in the MS drainage is similar, sometimes even lower than that in the streams. The dissolved Zn concentrations in the drainage waters and in the streams indicate an increasing tendency with DOC, with in particular high DOC and high Zn in the drainage at the OS site (Figure 1). However, total dissolved Zn and DOC are not well correlated with each other. Therefore, dissolved organic carbon may promote Zn solubility and mobility but its impact is not so strong to neglect other effects.

Zn speciation in the water samples (Tables II, III) varies largely with environmental conditions, such as pH, alkalinity, DOC etc. A substantial part of Zn is present in weaker organic or inorganic complexes, which are measured as ASV labile. The labile fraction varies widely, 3–30% in the Kleine Aa and 6–20% in the OS drainage, and non-labile complexes range from 70 to 95% of total dissolved Zn in the Kleine Aa and the drainage waters (with one exception from MS drainage). The Zn-inorganic complexes only play a minor role, with calculated inorganic complexation coefficients including hydroxyl and carbonate complexes, ranging from 1 to 4 for the stream waters, 0.4 to 1 for MS drainage and 0.04 to 0.09 for OS drainage. In all samples, the labile organic complexes are a small fraction, and free $[Zn^{2+}]$ is in the range 1–17% of the dissolved Zn with exception of one high value (40%) from MS drainage. The fraction of $[Zn^{2+}]$ in the OS drainage is about 3 times higher, in most cases, than in the stream waters, although DOC is higher in the OS drainage, but higher $[Zn^{2+}]$ may be attributed to lower pH in the drainage water. If compared between the two streams at the same date, the fraction of labile or free ionic Zn to total dissolved Zn is generally higher

Table II. Dissolved Zn speciation in the drainage waters of MS and OS soils

Sampling site drainage	Sampling date	Working pH	DOC mg/l	Total diss. $[Zn]_t$ M	Labile $[Zn]_0$. M	Strong $[ZnL_1]org$ M	Weak $[ZnL_2]org$ M	Ambient $[Zn^{2+}]$ M	Inorg $[ZnI]_{inorg}$ M	*pZn*	Labile $[Zn]_0$. %Zn(tot)	Strong $[ZnL_1]org$ %Zn(tot)	Weak $[ZnL_2]org$ %Zn(tot)	Ambient $[Zn^{2+}]$ %Zn(tot)	Inorg. $[ZnI]_{inorg}$ %Zn(tot)
MS	4-Oct-99	7.09	2.7	2.45E−08	1.32E−09	2.32E−08	1.61E−10	7.83E−10	3.80E−10	9.1	5.4	94.6	0.7	3.2	1.6
MS	25-Oct-99			no drainage							no drainage				
MS	9-Nov-99	6.92	4.7	6.88E−08	1.21E−08	5.67E−08	8.95E−11	8.50E−09	3.55E−09	8.1	17.6	82.4	0.1	12.3	5.2
MS	24-Nov-99	7.22	2.6	4.74E−08	1.12E−08	3.63E−08	0.00E+00	6.21E−09	5.28E−09	8.2	23.5	76.5	0.0	13.1	11.1
MS	31-Jan-00			no drainage							no drainage				
MS	14-Feb-00	7.43	2.2	3.06E−09	3.00E−09	5.81E−11	5.70E−10	1.23E−09	1.20E−09	8.9	98.1	1.9	18.6	40.1	39.2
OS	4-Oct-99	6.29	32.8	9.33E−08	1.58E−08	7.75E−08	0.00E+00	1.40E−08	1.77E−09	7.9	16.9	83.1	0.0	15.0	1.9
OS	25-Oct-99			no drainage							no drainage				
OS	9-Nov-99	6.31	20.3	3.26E−07	5.40E−08	2.71E−07	4.95E−08	4.29E−09	1.96*E*−10	8.4	16.6	83.2	15.2	1.3	0.1
OS	24-Nov-99	6.77	42.4	3.15E−07	1.85E−08	2.97E−07					5.9	94.1			
OS	31-Jan-00	6.60	39.2	2.65E−07	5.40E−08	2.11E−07	9.14E−09	4.29E−08	1.96E−09	7.4	20.4	79.6	3.5	16.2	0.7
OS	14-Feb-00	6.73	38.0	3.35E−07	5.65E−08	2.79E−07	0.00E+00	5.17E−08	4.76E−09	7.3	16.9	83.1	0.0	15.4	1.4

Table III. Dissolved Zn speciation in the streams from Sempach catchment

Sampling site streams	Sampling date	Working pH	DOC mg/L	Total diss. $[Zn]_t$ M	Labile $[Zn]_0$. M	Strong $[ZnL_1]org$ M	Weak $[ZnL_2]org$ M	Ambient $[Zn^{2+}]$ M	Inorg $[ZnI]_{inorg}$ M	*pZn*	Labile $[Zn]_0$. %Zn(tot)	Strong $[ZnL_1]org$ %Zn(tot)	Weak $[ZnL_2]org$ %Zn(tot)	Ambient $[Zn^{2+}]$ %Zn (tot)	Inorg. $[ZnI]_{inorg}$ %Zn(tot)
Kleine Aa	4-Oct-99	8.32	5.6	3.52E−08	3.37E−09	3.18E−08	0.00E + 00	8.78E−10	2.49E−09	9.1	9.6	90.4	0.0	2.5	7.1
Kleine Aa	25-Oct-99	8.36	4.6	2.22E−07	7.76E−09	2.15E−07	1.70E−10	3.52E−09	4.07E−09	8.5	3.5	96.8	0.1	1.6	1.8
Kleine Aa	9-Nov-99	8.14	8.7	9.79E−08	4.20E−09	9.37E−08	9.35E−10	1.70E−09	1.56E−09	8.8	4.3	95.7	1.0	1.7	1.6
Kleine Aa	24-Nov-99	8.44	4.8	3.52E−08	9.88E−09	2.53E−08	1.69E−09	2.20E−09	5.98E−09	8.7	28.1	71.9	4.8	6.3	17.0
Kleine Aa	31-Jan-00		4.8	1.84E−08	not measured										
Kleine Aa	14-Feb-00	8.47	4.4	1.99E−08	4.25E−09	1.56E−08	9.60E−10	6.52E−10	2.64E−09	9.2	21.4	78.6	4.8	3.3	13.3
Greuelbach	4-Oct-99	8.42	2.1	2.45E−08	3.33E−09	2.11E−08	0.00E + 00	1.18E−09	2.16E−09	8.9	13.6	86.4	0.0	4.8	8.8
Greuelbach	25-Oct-99	8.34	1.8	2.45E−07	3.45E−09	2.41E−07	0.00E + 00	1.07E−09	2.38E−09	9.0	1.4	98.5	0.0	0.4	1.0
Greuelbach	9-Nov-99	8.39	2.9	5.05E−08	7.52E−09	4.30E−08	0.00E + 00	1.82E−09	5.70E−09	8.7	14.9	85.1	0.0	3.6	11.3
Greuelbach	24-Nov-99	8.38	2.6	2.60E−08	1.43E−08	1.17E−08	8.32E−09	1.55E−09	4.40E−09	8.8	54.9	45.1	32.0	6.0	16.9
Greuelbach	31-Jan-00		1.5	3.06E−09	not measured										
Greuelbach	14-Feb-00	8.39	1.5	9.18E−10	5.98E−10	3.20E−10	0.00E + 00	1.55E−10	4.43E−10	9.8	65.2	34.8	0.0	16.9	48.3

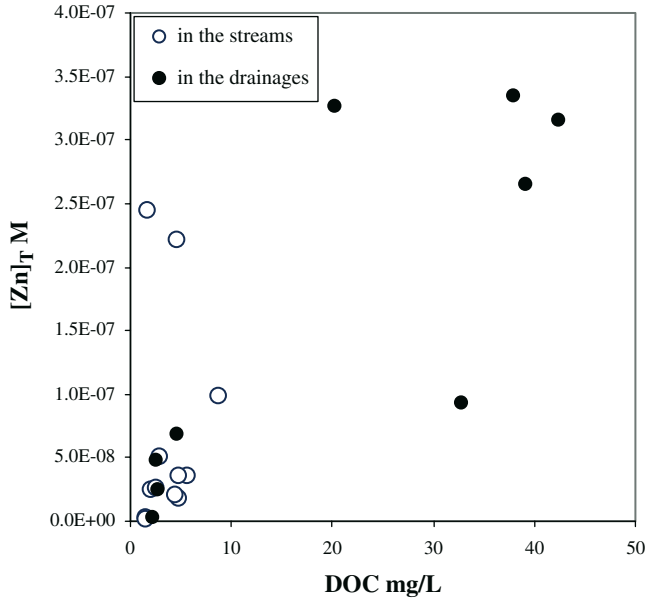

Figure 1. Dissolved zinc as a function of DOC in the stream and the drainage waters.

in the Greuelbach than in the Kleine Aa (with one exception), in agreement with lower DOC at a similar pH in Greuelbach. The higher total dissolved Zn and higher free Zn^{2+} fraction result in much higher $[Zn^{2+}]$ (pZn 7.3–7.9) in the OS drainage than those in the streams (pZn 8.5–9.1) and in the MS drainage (pZn 8.1–9.1).

The fraction of labile Zn and of free Zn ion is sensitive to environmental conditions, especially to the DOC concentration. Therefore, generally Zn speciation is controlled by Zn-organic complexation. The ratio of $[Zn^{2+}]$ or $[Zn]_{lab}$ to $[Zn]_T$ is related to DOC (Figure 2a). The determined $[Zn^{2+}]/[Zn]_T$ ratios dramatically decrease with increasing DOC up to 5 mg/L of DOC. For DOC $>$ 5 mg/L the ratios $[Zn^{2+}]/[Zn]_T$ are low. The extent of complexation also depends on pH and other environmental conditions. For example, the organic carbon concentrations in the MS drainage are similar as in the streams, but the ratios of $[Zn^{2+}]$ to total dissolved Zn are generally higher than those in the streams, which could be partially attributed to about one unit lower pH.

The ligand-exchange method to determine free ionic Zn concentrations may be subject to some errors. If the ligand-exchange reactions did not reach equilibrium, then [ZnEDTA] and consequently $[Zn^{2+}]$ may be underestimated. The exchange equilibration can generally be reached for 10 h in river or lake waters (Xue and Sigg, 1994). However, very slow ligand exchange for Zn complexation could occur in such drainage waters with higher organic

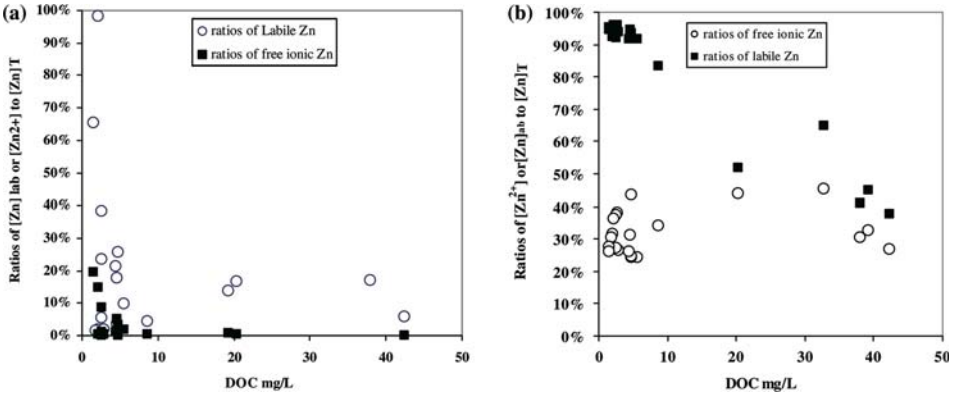

Figure 2. Ratios of $[Zn^{2+}]$ or $[Zn]_{lab}$ to $[Zn]_T$ as function of DOC in the stream and the drainage waters; (a): measured results and (b): simulated results (from WHAM VI model).

matter, and Fe (Xue et al., 1995b). For example, the OS drainage water of 9 November gives only 1.3% of total dissolved Zn as $[Zn^{2+}]$, relatively lower than others with similar pH, DOC and labile fractions, which may be due to lack of equilibration of ligand exchange. Nevertheless, no indications of slow exchange reactions were observed during the measurement. The highest phosphorus content of this drainage water among all samples (Table I) originated from intensive application of livestock manure containing high P and N, as well as fresh organic matter. Very slow exchange reactions of Zn may occur between freshly introduced organic ligands and soil organic ligands, as well as after EDTA addition. In such a sample, the content of weak organic complexes (ZnL_2) may be overestimated.

A conditional stability constant for non-labile complexes (ZnL_1) could be evaluated by fitting a data set of $[Zn^{2+}]$ and $[ZnL_1]$ ($=[Zn]_T - [Zn]_{lab} - [ZnEDTA]$) while titrating with Zn. In this study, the stability constant was not evaluated because only few titration points were obtained in the presence of EDTA. The stability constants of Zn strong complexes have been found to be in the range log K $\approx$ 8–9 in lake or river waters (Xue et al., 1995a) and in the same range (log K 8.7–8.8) in drainage waters from another catchment (Aldrich et al., 2002) and are 3 to 6 orders of magnitude lower than those of Cu organic complexes.

3.2. MODELING ZN SPECIATION IN THE RIVER AND DRAINAGE WATERS

The simulated Zn speciation using the WHAM VI model is plotted in Figure 3. In the simulations, FA-bound Zn is assumed to represent the organic complexes, and amounts to 35–62% of Zn_T for the OS drainage, 4.1–6.6% for the MS drainage and 4.8–16.6% for the stream waters. These

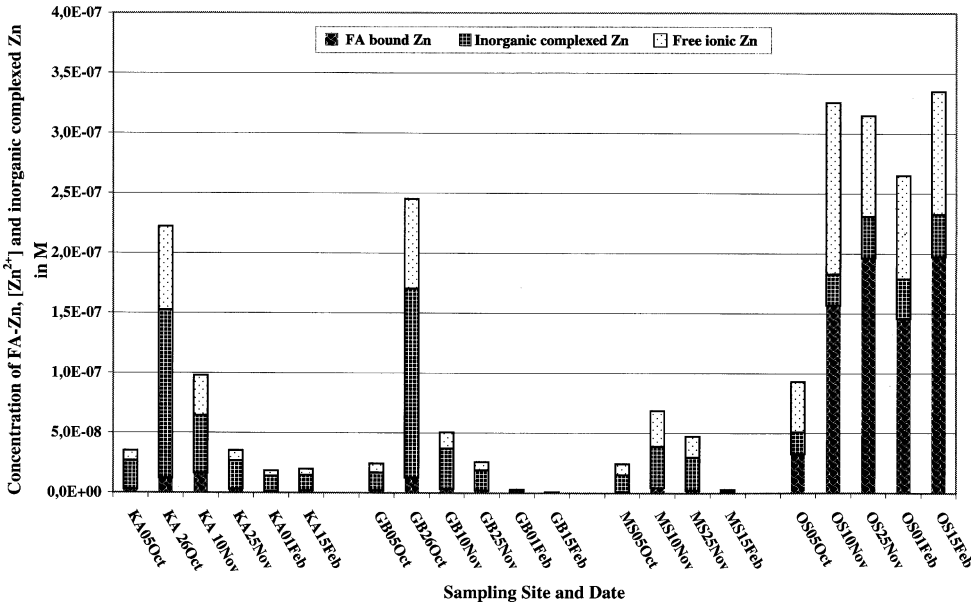

Figure 3. WHAM VI simulated Zn distribution among FA-bound, inorganic complexes and free ionic Zn in the stream and the drainage waters.

concentrations of FA-bound Zn are compared with the experimentally obtained non-labile complexes. Although the simulated FA-bound Zn is much higher in the OS drainage than in the stream waters, the simulated bound fractions in all the samples are lower than the measured fractions of non-labile Zn complexes (strong ZnL_1), with only one exception from MS drainage. If we take into account the measured weak organic complexes (ZnL_2), differences between the simulated FA-bound Zn and the measured Zn-organic complexes are even larger. The simulation also results in higher simulated free Zn^{2+} concentrations than the experimental ones (Figure 4). The difference of the simulated and the measured $[Zn^{2+}]$ is in average 0.78 ± 0.39 pZn units and the root-mean-square residue (RMSR) 0.92 pZn unit. The simulated ratio of $[Zn^{2+}]/[Zn]_T$ or $[Zn]_{lab}/[Zn]_T$ as a function of DOC also shows different patterns than the measured fraction (Figure 2a, b). The difference in the dependency on DOC is probably due to the presence of stronger ligands at low DOC. The modeled Fe(III) speciation indicates that most of iron is bond in colloidal FA, especially in the OS drainage. Binding of Fe(III) may thus compete with Zn binding.

In general, the organic complexed species are far less significant for Zn than it has been observed for Cu in soil solutions (Weng et al., 2002). Weng et al. (2002) measured $[Zn^{2+}]$ in $Ca(NO_3)_2$-extracted solution from soil columns by Donnan membrane and compared those with simulated results by

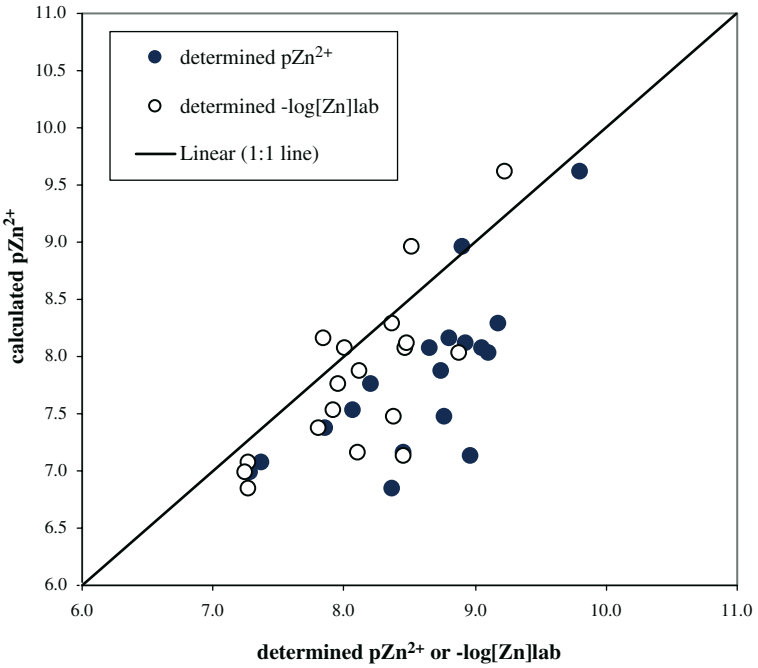

Figure 4. Calculated [Zn^{2+}] modeled with WHAM VI in comparison to the analytically determined [Zn^{2+}] in the stream and the drainage waters.

the WHAM VI and NICA-Donnan models (Kinnburgh et al., 1999). They also obtained lower measured [Zn^{2+}] than simulated free Zn^{2+}, but with a better agreement than in the present work. Discrepancy between the present study and the study by Weng et al. (2002) may be attributed to different analytical techniques for [Zn^{2+}], different soil composition and solution conditions and different modeling assumptions. Weng et al. (2002) used extracted soil solutions with lower pH and higher total dissolved Zn concentration. Their simulation indicated that the WHAM VI model resulted in weaker organic binding than the NICA-Donnan model, and that WHAM is insensitive to different combination of FA and HA. Therefore, assumed variations in DOC composition with different FA and HA would not help to improve our simulated results.

The discrepancies in Zn speciation between the determined results and predictions from the simulation of WHAM VI model may originate from both analytical uncertainties and modeling assumptions. Considering that the analytical technique may overestimate the binding strength, we also plotted the determined labile Zn in Figure 4 to compare with the simulated free Zn. Most of the determined labile Zn concentrations are still lower than the simulated free Zn ionic concentrations, but are closer to the simulated [Zn^{2+}]. The difference for the simulated [Zn^{2+}] and measured $[Zn]_{lab}$ gives an

improved result (difference 0.33 log unit in average). However, the analytically determined labile Zn includes free Zn^{2+} ion, inorganic species and weak organic complexes and should be always higher than free Zn^{2+}. Therefore the biases of the model results may rather be attributed to simulation assumptions or model constants. The WHAM VI constants are "best-average" values from isolated FA, which may not be fully representative of the dissolved organic matter in the field. The drainages leached from the soils after excess application of animal manures, especially the OS drainage. The organic matter in the soil leachates may not be fully humified, with fresh manures that may contain organic matter with higher affinity for metal complexation than isolated FA.

3.3. EFFECTS OF THE SOIL COMPOSITION ON ZN SPECIATION AND TRANSPORT

Metal speciation in soil drainage is related to the composition of the drainage and thus to the equilibration with the soil solid phase. A previous publication (Xue et al., 2003) indicates that the Zn contents in the soil columns are different in the MS and OS sites, with ratios of Zn to NOM of 0.13 μmol Zn/mmol C at the OS site, 0.50 μmol Zn/mmol C at the MS site (increasing with depth from 0.38 to 0.61) and that the ratio of water-extractable Zn from soil columns at both sites are the same with 0.23 μmol Zn per mmol C. The Zn inputs to the two different soils of the OS site and MS site should be the same, as these sites are located within short distance. In the mineral soil (MS), the contribution of inorganic material like clay silicates and iron oxides to Zn binding may be more important (Weng et al., 2001). Zn accumulation during a long period in the mineral soil at the MS sites may lead to Zn being tightly sorbed into the internal structure of minerals, which may not be easily desorbed by binding to dissolved organic ligands. Therefore, Zn solubility may be mainly controlled by distribution of NOM between solid and soluble phases directly at the OS site, but at the MS sites is influenced by the retention in mineral phases because of the lower NOM content. On the other hand for the same area the ratio of Cu and NOM is the same in both soil columns with 0.15 μmol Cu/mmol C, also the ratio of extractable Cu to extractable DOC is the same at both sites with 0.25 μmol Cu/mmol C, indicating a similar Cu retention and a similar solubility by the soil organic matter at the two sites. These ratios indicate that more Zn is released from the OS soil, due to higher concentration of DOC in the OS drainage than in the MS drainage. The Zn organic complexes in solutions are weaker than the Cu complexes, moreover a substantial fraction of the dissolved Zn is present as weak organic and inorganic complexes or free ionic Zn. Zinc binding to organic matter in the solid phase is probably also weaker.

The water content of the soil column at the OS site is relatively higher, 60–70% of total weight, whereas it is about 20% of total soil weight at the MS sites in the collected samples. The Zn accumulation is in the OS soil column only about half of that in the MS soil column, which is overcompensated by the 7–8 times higher Zn concentration in the OS drainage than in the MS drainage (Table II), resulting in greater loss of Zn from the OS site. Therefore, the OS soil contributes about twice as much Zn input to the receiving water in Kleine Aa than the MS soil as related to the specific area (Xue et al., 2003).The mobility of Zn in soil depends on the competition between binding to the solid matrix and binding by dissolved organic ligands (Buerge-Weirich et al., 2002). Clearly the loss of Zn has been facilitated by higher organic matter content in the soil, the high concentration of DOC and high water content at the OS site. The mineral soil with less OS and less water content in the soil column and less DOC in the soil solution could retain more Zn for a longer period.

The organic soil because of its high organic matter content retains large amount of water. As a result the organic soil continues to drain for longer periods compared to the mineral soil and contributes a large fraction to the total river discharge during extended drainage periods, in which the drainage water also contains higher metal concentrations. The different speciation and migration behavior of Zn from two different soils thus originate from different contents and distribution of organic matter between soil solid phase and solution. The mobility of Zn from agricultural soils appears to strongly depend on the organic matter content and on the affinity of the organic matter for Zn complexation. Organic Zn complexes in solution contribute to facilitate Zn transport from soil into drainage water and subsequently to surface waters.

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